

Final Technical Report

**Shock Tube Measurements of Ignition Processes
in Diesel-Related Fuels and Additives**

Submitted to

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Submitted by

**Professor R. K. Hanson
Dr. D. F. Davidson
Mechanical Engineering Department
Stanford University**

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Abstract

Results of a three-year program of basic research aimed at improving knowledge of the combustion kinetics behavior of diesel-related fuels are reported. The work is intended to develop a database of gas-phase chemical kinetic and two-phase spray reference measurements applicable to improving diesel engine modeling and performance. Research was conducted in two Stanford shock tube facilities and focused on two topics: (1) measurements of shock-induced ignition time and individual species concentration time-histories measurements during the combustion of diesel-related gas-phase fuels, and (2) fundamental studies of fuel sprays in a new aerosol shock tube using state-of-the-art optical diagnostic techniques.

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Figure 2. OH concentration time-history data: toluene ignition. Initial shock conditions: 1648 K, 2.0 atm, 250 ppm toluene, 2250 ppm O₂, balance Ar. The modified LLNL OH profile includes changes to the LLNL mechanism recommended in Venkatesh et al. (2004).

Figure 3. Correlated branched-alkane ignition times. All data normalized to 1 atm, $\Phi = 1$, and 21% O₂. Filled squares, iso-butane; open circles, iso-pentane; filled triangles, iso-octane; lines, correlations.

Figure 4. Iso-butane OH absorption data. Initial conditions: 0.1% iso-butane, 0.65% O₂. Upper trace 1720 K, lower trace 1411 K. Strong suppression of OH radical populations during the induction period before ignition is evident in the 1411 to 1593 K data.

Figure 5. OH concentration time-histories in these experiments were measured using narrow-linewidth ring-dye laser absorption at 306.5 nm in a shock tube. The OH concentration plateau is suppressed before ignition in the iso-octane experiments, but not in the n-heptane experiments.

Figure 6. OH concentration time-history: 1,3-butadiene oxidation. The rapid formation of OH seen in the current data supports the new 1,3-butadiene decomposition pathways proposed by Laskin, Wang and Law (2000).

Figure 7. Ignition delay time measurements: 1,3-butadiene. The current measurements are in agreement with the modeling of Laskin, Wang and Law (2000).

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Figure 10. Cross-sectional illustration of the diagnostic setup, looking toward the endwall. Six lasers pass through the test section, thus giving line-of-sight information about the particle size distribution, gas temperature, and vapor pressure.

Figure 11. Typical measurement of particle loading in a shock experiment. Shock conditions: $T_1 = 293$ K, $P_1 = 0.266$ atm, $T_2 = 549$ K, $P_2 = 1.102$ atm, $T_5 = 856$ K, $P_5 = 3.362$ atm. The blue lines indicate the ideal gas density increases across the shocks.

Figure 12. Rate coefficients derived from shock tube experiments for the D² evaporation law for water and dodecane.

Statement of the Problem Studied

The work described in this report covers a three year program of research into the ignition processes of diesel-related fuels in shock tubes and was comprised of two parts: A) the study gas-phase diesel-related fuel ignition times and species concentration time-histories and their application to the validation and refinement of reaction mechanisms; and B) the study of the interaction of fuel sprays with shock waves in a unique new spray/shock interaction facility.

Gas-Phase Diesel Chemistry

One of the primary goals of this ARO contract was to develop an extensive, high-quality database of ignition time measurements and species concentration time-histories useful for the validation of chemical kinetic models of hydrocarbon oxidation. These studies allow us to: 1) provide reliable target data for the validation of chemical kinetics models of ignition; 2) develop ignition time correlations to summarize the wide range of data; 3) critically review the existing ignition time literature for these hydrocarbon fuels, and 4) identify, and if possible, measure key reactions needed to reduce the uncertainty in the predictions of these mechanisms.

One set of these kinetic targets, the OH concentration time-history data, are unique, and offer the combustion modeler the first quantitative glimpse into the kinetics of the small radical pool (H, O, OH) that plays a critical role in the ignition process. Time-resolved measurements of OH radicals, for example, have provided the first direct experimental evidence of the theoretically-predicted radical suppression found in branched-alkane oxidation, but not in n-alkane oxidation, Davidson et al. (2002), and have helped identify deficiencies in the initial decomposition pathways and rates in some models of 1,3-butadiene oxidation, Libby et al. (2004). More generally, these OH measurements provide quantitative measurements of the radical concentration levels and temporal behavior that occur during the multiple phases of oxidation, i.e., the initial fuel decomposition, the initial OH plateau or suppression period, the "ignition" phase, the peak levels of OH, and the final approach of OH to equilibrium. With these data, modelers will be able to refine their mechanisms based on actual radical chemistry measurements rather than using only macroscopic engineering parameters, such as ignition times and concentrations of stable combustion products.

Aerosol Shock Tube for Spray-Shock Wave Interaction Studies

There is a critical need for high-quality, modern experimental data describing shock wave and detonation wave interactions with fuel sprays for use as targets for CFD model computations. Facilities for these experiments do not exist at present, and we were unaware of any fundamental data on the interaction of heterogeneous flows with shocks and detonation waves acquired with modern imaging and line-of-sight optical and spectroscopic diagnostics.

We proposed to use a unique test apparatus, an aerosol shock tube, to enable investigations of the interaction of shock waves and detonation waves with fuel sprays. This test apparatus was built from an existing shock tube facility and has permitted the propagation of incident and reflected shock waves and shock-induced detonation waves in spray-air mixtures. There are, to our knowledge, no currently operating facilities with the capability to address these fundamental heterogeneous flows using modern optical diagnostics.

The findings from such experiments are relevant to the analysis and modeling of future air-breathing engines, and will provide data needed to guide and validate CFD analyses of air-breathing propulsion systems with these flow elements. The importance of reliable, accurate and detailed experimental data for CFD modeling cannot be overemphasized. Comparison of CFD computations with such heterogeneous flow data will permit exacting constraints on spray-interaction models and on shock wave and detonation wave structure models. A much stronger reliance on the results of CFD computations for such flows should then be possible.

Summary of the Most Important Results

High pressure iso-octane/air and toluene/air ignition delay time measurements

Ignition times were measured in a shock tube for iso-octane/air and toluene/air at high pressures. Initial reflected shock conditions spanned the following ranges: temperature 855 – 1269 K, pressure 14 to 59 atm, and equivalence ratios of 0.5 and 1 in synthetic air. Ignition times were measured using sidewall pressure via piezo-electric transducers and confirmed with OH* and CH* emission measurements. The iso-octane ignition times are in excellent agreement with existing measurements by Fieweger et al. (1994, 1997) and modeling by Ogink and Golovitchev (2001) (Chalmers University). No comparable high-pressure data exists for toluene/air, and modeling by Pitz et al. (2001) significantly overpredicts the toluene/air ignition times. The large pressure range of the current measurements permits determination of the pressure dependence of ignition time at the temperatures and pressures of direct interest in HCCI engine simulations. Detailed examination of the pressure-time profiles shows evidence of significant pre-ignition energy release in both the iso-octane/air and toluene/air systems. Example data is shown in Fig. 1. Using current detailed mechanisms, the rate of this energy release is not correctly predicted in either iso-octane/air or toluene/air at temperatures above 850 K. This work is described in Davidson, Gauthier and Hanson, in press.

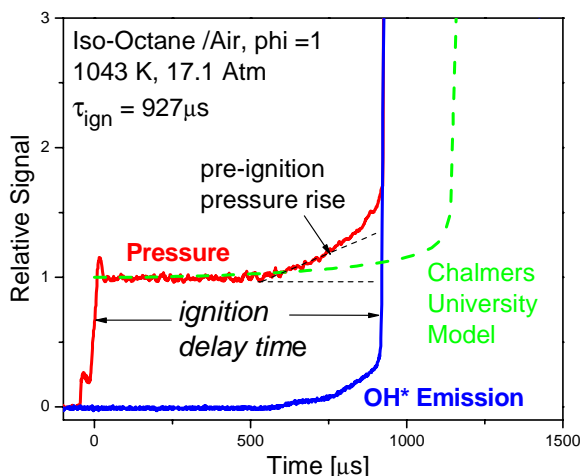


Figure 1. Pressure time-history data: iso-octane ignition. Initial shock conditions: 1043 K, 17.1 atm, 1.68% iso-octane, 21% O₂, balance N₂. Pre-ignition energy release is evident in the pressure trace and similar behavior is seen in the OH* emission trace.

Toluene/O₂/Ar ignition delay time and OH concentration measurements

Ignition delay times and OH radical concentration profiles were measured in toluene/O₂/Ar mixtures behind reflected shock waves. Initial reflected shock conditions spanned 1400 - 2000 K and 1.5 - 5.0 atm, with equivalence ratios of 0.5 - 1.875 and toluene concentrations of 0.025 - 0.5%. OH time-histories were monitored using narrow-linewidth ring dye laser absorption of the well-characterized R₁ (5) line of the OH A-X (0, 0) band at 306.7 nm.

Ignition time data was extracted from the OH traces and was found to compare very well with measurements using sidewall pressure. These new data are in agreement with the recent measurements of Burcat et al. (1986), but not with the measurements of Pitz et al. (2001) or Burcat et al. (1979). The results of this study were compared to three detailed kinetic models: Pitz et al. (2001) (LLNL), Dagaut et al. (2002) and Lindstedt et al. (1996). The ability of the mechanisms to predict the measured ignition time data and OH concentration profiles was analyzed. Suggestions to improve model performance have been made, and key reactions that need to be studied further have been identified. This work has yielded the first quantitative measurements of OH time-histories during toluene oxidation, and hence provides a critical data set useful for evaluating and refining comprehensive mechanisms on toluene oxidation. Example data is shown in Fig. 2. This work is described in Venkatesh et al., in press.

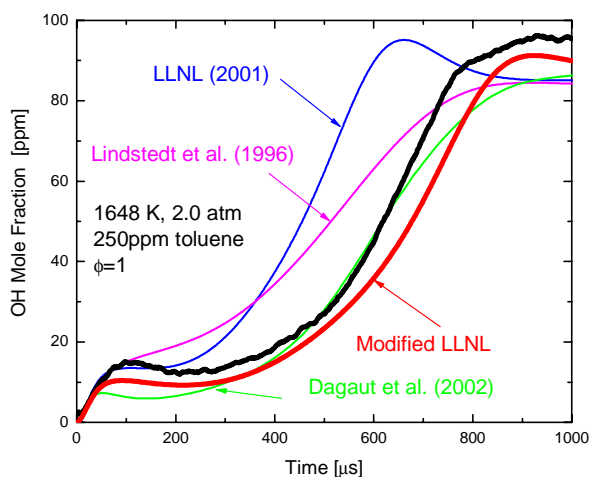


Figure 2. OH concentration time-history data: toluene ignition. Initial shock conditions: 1648 K, 2.0 atm, 250 ppm toluene, 2250 ppm O₂, balance Ar. The modified LLNL OH profile includes changes to the LLNL mechanism recommended in Venkatesh et al. (2004).

Interpreting shock tube ignition data

Chemical kinetic modelers make extensive use of shock tube ignition data in the development and validation of combustion reaction mechanisms. These data come from measurements using a range of diagnostics and a variety of shock tubes, fuels, and initial conditions. With the wide selection of data available, it is evident that not all of the data are of all the same type or quality, nor are all the data suitable for simple, direct comparison with the predictions of reaction mechanisms. We developed some guidelines for the comparison of shock tube ignition time data with reaction mechanism modeling. Areas discussed include: definitions of ignition time; ignition time correlations (with examples taken from recent n-heptane and iso-octane measurements); shock tube constant-volume behavior; shock tube diameter and boundary layer effects; carrier gas and impurity effects; and future needs and challenges in shock tube research. This work is described in Davidson and Hanson (2004).

Branched alkane ignition delay times and OH concentration time-history measurements

Ignition times and hydroxyl (OH) radical concentration time-histories were measured behind reflected shock waves during the oxidation of three branched alkanes: iso-butane (2-methylpropane), iso-pentane (2-methylbutane), and iso-octane (2,2,4-trimethylpentane.) (The iso-octane data are described separately below.) Initial reflected shock conditions ranged from 1177 to 2009 K and 1.10 to 12.58 atm with dilute fuel/O₂/Ar mixtures varying in fuel concentration from 100 ppm to 1.25% and in equivalence ratio from 0.25 to 2. Ignition times were measured using endwall CH emission and OH concentrations were measured using narrow-linewidth ring-dye laser absorption of the R₁(5) line of the OH A-X (0,0) band at 306.7 nm. Example ignition time data are shown in Fig. 3 and example OH concentration data for iso-butane oxidation are shown in Fig. 4. Correlations based on these ignition time measurements are:

$$\text{iso-butane (58 points): } \tau_{\text{ign}} = 6.90 \times 10^{-12} P^{-0.33} X_{\text{O}_2}^{-0.42} \Phi^{0.97} \exp(48560 [\text{cal/mol}]/RT)$$

$$\text{iso-pentane (34 points): } \tau_{\text{ign}} = 2.63 \times 10^{-12} P^{-0.59} X_{\text{O}_2}^{-0.61} \Phi^{1.30} \exp(49450 [\text{cal/mol}]/RT)$$

$$\text{iso-octane (95 points): } \tau_{\text{ign}} = 4.50 \times 10^{-10} P^{-0.56} \exp(-18.6 X_{\text{O}_2}) \Phi^{1.62} \exp(44780 [\text{cal/mol}]/RT)$$

with ignition time τ_{ign} in s, pressure P in atm, oxygen mole fraction X_{O_2} , equivalence ratio Φ , activation energy E_A in cal/mol, and temperature T in K. The ignition times and OH concentration time-histories were compared to modeled predictions of seven branched alkane oxidation mechanisms currently available in the literature and the implications of these comparisons are discussed. These data provide a unique database for the validation of detailed hydrocarbon oxidation mechanisms of propulsion related fuels. This work is described in Oehlschlaeger et al. (2004).

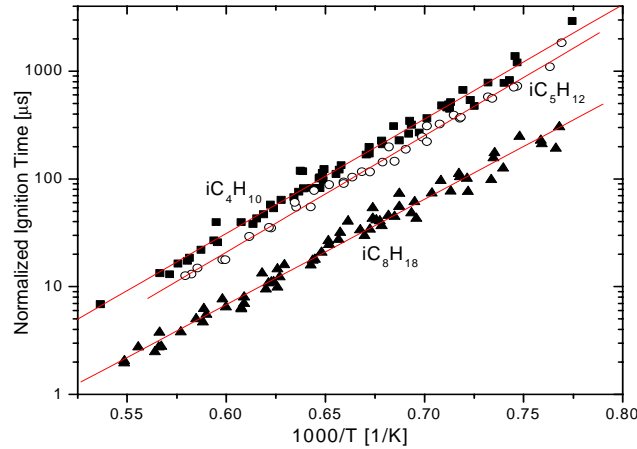


Figure 3. Correlated branched-alkane ignition times. All data normalized to 1 atm, $\Phi = 1$, and 21% O₂. Filled squares, iso-butane; open circles, iso-pentane; filled triangles, iso-octane; lines, correlations.

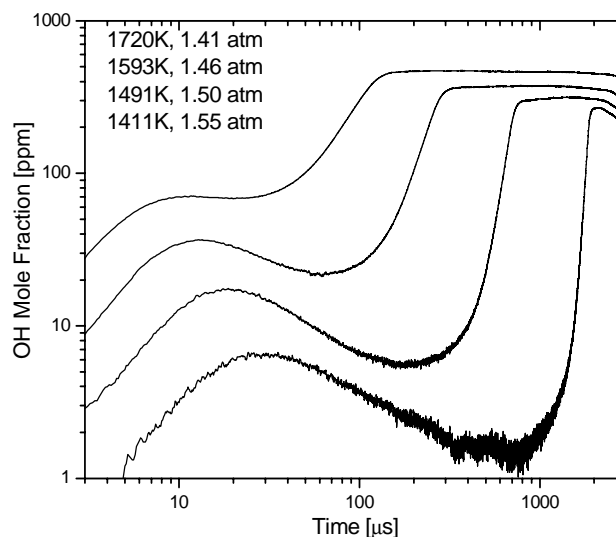


Figure 4. Iso-butane OH absorption data. Initial conditions: 0.1% iso-butane, 0.65% O₂. Upper trace 1720 K, lower trace 1411 K. Strong suppression of OH radical populations during the induction period before ignition is evident in the 1411 to 1593 K data.

Iso-octane ignition delay time and OH concentration measurements

Ignition times and OH radical concentration time-histories were measured behind reflected shock waves in iso-octane/O₂/Ar mixtures. Initial reflected shock conditions were in the ranges 1177 to 2009 K and 1.18 to 8.17 atm, with fuel concentrations of 100 ppm to 1% and equivalence ratios from 0.25 to 2. Ignition times were measured using endwall emission of CH and sidewall pressure. OH concentrations were measured using narrow-linewidth ring-dye laser absorption of the R₁(5) line of the OH A-X (0,0) band at 306.5 nm. The ignition time data and OH concentration time-history measurements were compared to model predictions of four current iso-octane oxidation mechanisms, and the implications of these comparisons are discussed. A comparison of the OH concentration time-histories for iso-octane and n-heptane are shown in Fig. 5. To our knowledge, these data provide the first extensive measurements of low fuel-concentration ignition times and OH concentration time-histories for iso-octane auto-ignition, and hence provide a critical contribution to the database needed for validation of a detailed mechanism for this primary reference fuel. This work is described in Davidson et al. (2002).

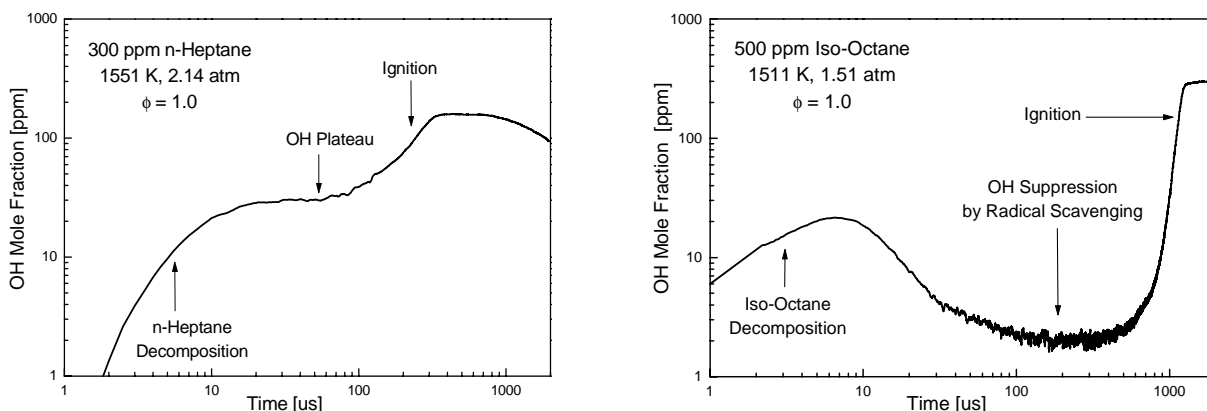


Figure 5. OH concentration time-histories in these experiments were measured using narrow-linewidth ring-dye laser absorption at 306.5 nm in a shock tube. The OH concentration plateau is suppressed before ignition in the iso-octane experiments, but not in the n-heptane experiments.

n-Alkane ignition delay time measurements

Ignition time measurements of propane, *n*-butane, *n*-heptane and *n*-decane have been studied behind reflected shock waves over the temperature range of 1300-1700 K and pressure range of 1-6 atm. The test mixture composition varied from approximately 2-20% O₂, and the equivalence ratio ranged from 0.5 to 2.0. To more precisely determine the fuel mole fraction of the test mixture, a new technique has been employed in which a 3.39 μm HeNe laser and multiple-pass set-up is utilized to measure the fuel in-situ by absorption. Ignition delay times were measured at the shock tube endwall by a CH emission diagnostic (431 nm) that viewed the shock-heated mixture through a window in the endwall. This enabled the ignition time at the unperturbed endwall conditions to be accurately determined, thereby avoiding problems inherent in measuring ignition times from the shock tube sidewall. A parametric study of the experimental data reveals marked similarity of the ignition delay time characteristics among these four *n*-alkanes, and a unique correlation was developed in which the stoichiometric ignition time data for all four *n*-alkanes has been correlated into a single expression with an R² value of 0.992:

$$\text{n-alkanes: } \tau_{\text{ign}} = 9.4 \times 10^{-12} P^{-0.55} X_{\text{O}_2}^{-0.63} C^{-0.50} e^{46,550/RT}$$

where the ignition time is in seconds, pressure in atmospheres, the activation energy in cal/mol, X_{O₂} is the mole fraction of oxygen in the test mixture and C is the number of carbons atoms in the *n*-alkane. Comparisons to past ignition time studies and detailed kinetic mechanisms further validate this correlation. This work is described in Horning et al. (2002).

1,3-Butadiene ignition delay times and OH concentration time-history measurements

Hydroxyl (OH) radical concentration time-histories and ignition delay times were measured in dilute 1,3-butadiene/O₂/argon mixtures during reflected shock wave experiments. Initial shock conditions ranged from 1230 K to 1890 K and from 1.5 atm to 7.5 atm with fuel concentrations from 250 ppm to 5000 ppm and equivalence ratios from 0.25 to 2. OH

concentration histories were measured using narrow-linewidth laser absorption with the wavelength centered on the $R_1(5)$ line of the OH A-X (0,0) band at 306.7 nm. Ignition times were measured by OH absorption. Measured ignition times and OH concentration time-histories were compared to the predictions of four different 1,3-butadiene oxidation mechanisms currently found in the literature and to the results of one other shock tube study (Fournet et al. 1999). Example data is shown in Figs. 6 and 7. To our knowledge, this is the first shock tube study of 1,3-butadiene oxidation that includes quantitative measurements of a radical species time-history, and use of these data as kinetic targets should allow for a fuller validation of kinetic models for alkenes than through comparison with ignition time measurements alone. This work is described in Libby et al. (2004).

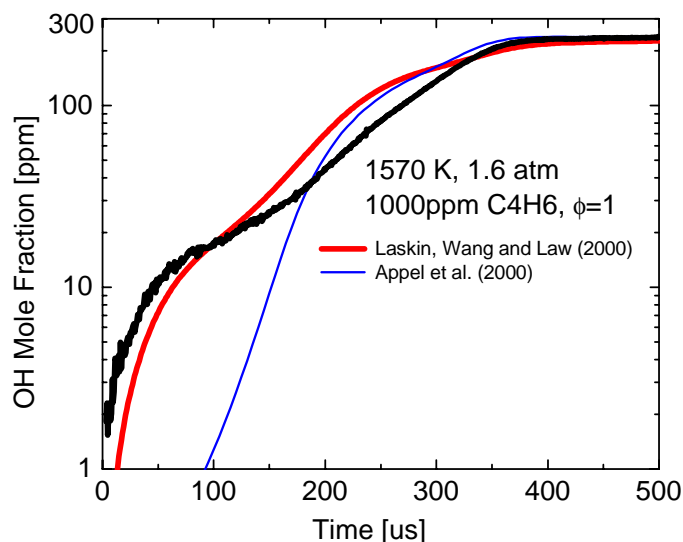


Figure 6. OH concentration time-history: 1,3-butadiene oxidation. The rapid formation of OH seen in the current data supports the new 1,3-butadiene decomposition pathways proposed by Laskin, Wang and Law (2000).

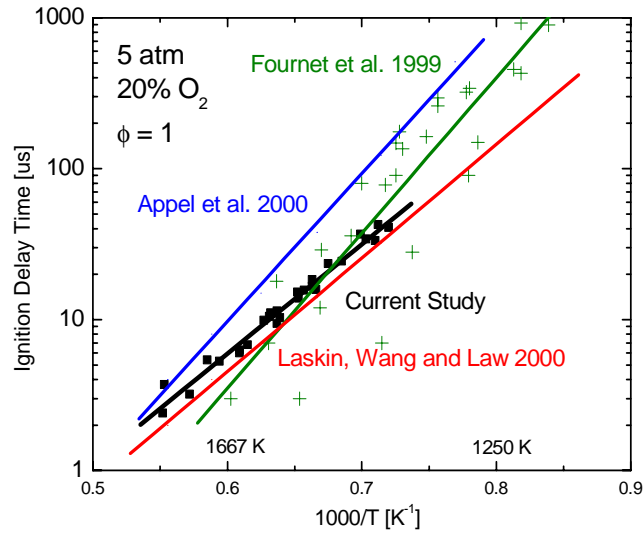


Figure 7. Ignition delay time measurements: 1,3-butadiene. The current measurements are in agreement with the modeling of Laskin, Wang and Law (2000).

Development of an aerosol shock tube

We have completed the construction of the new aerosol shock tube. The aerosol shock tube driver and driven lengths are 3.5 m and 9.6 m ($L/D = 84$), respectively, with an inside diameter of 114 mm. This facility enables experiments to be conducted in both the incident and reflected regions with temperatures in the range of 450-2500 K with test times between 500 μ s and 2 ms. A square cross-section section with the same cross-sectional area as the circular section provides line-of-sight access and 2-dimensional imaging access to the test section of the tube. An ultrasonic nebulizer produces droplets with D_{V50} near 3 microns that are admitted into the tube via four flush-mounted poppet valves in the endwall. The facility is shown in Figs. 8 and 9. This optically accessible shock tube has been specifically designed to facilitate fundamental studies of multiphase flows, droplet evaporation and ignition timescales, shock wave-induced combustion, and deflagration to detonation transitions. It will also serve as a useful facility for the development of new laser sensors for fast temperature, particle sizing and species concentration measurements. A time-resolved three-color laser extinction diagnostic has been developed to determine the droplet size distribution and loading. Using this diagnostic, measurements of the variation of the size distribution and loading of a water aerosol were made behind incident and reflected shocks. This work is described in Kashdan et al. (2004).

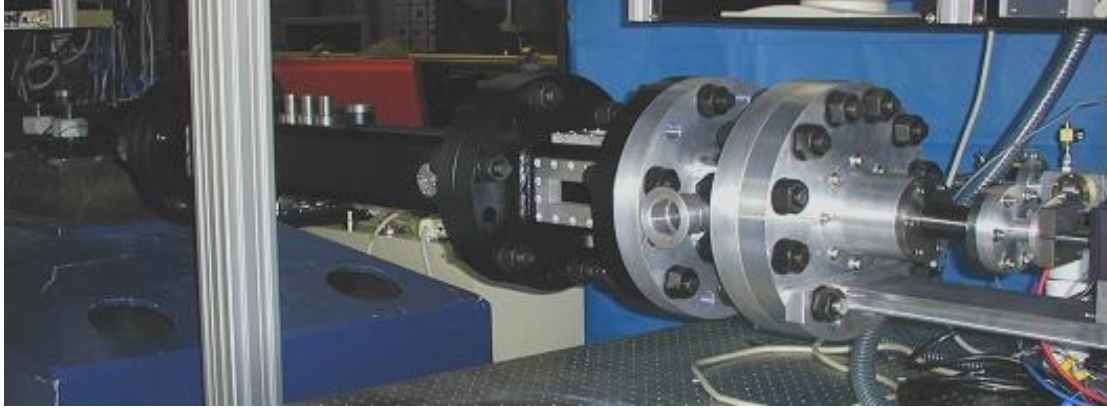


Figure 8. Detail of aerosol shock tube end section. The black epoxy coated pieces are the transition and viewing section; the aluminum section with black bolts houses the four flush-mounted poppet valves in the endwall.

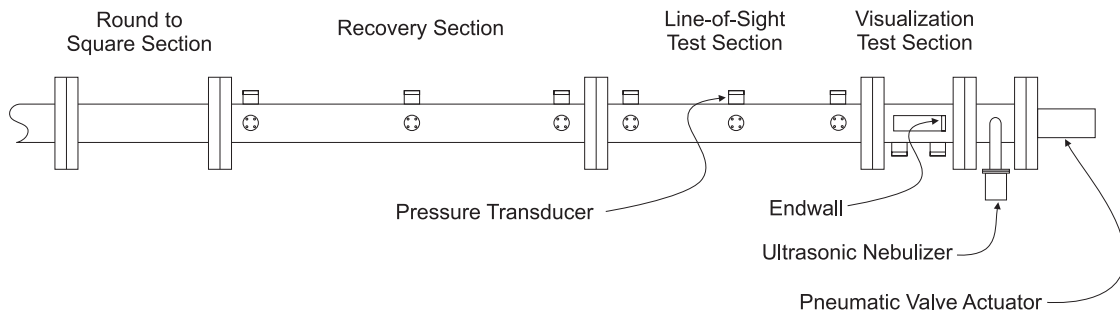


Figure 9. Schematic diagram of the aerosol shock tube showing the round-to-square transition, recovery section, line-of-sight test section, visualization section, endwall, valve system, and nebulizer.

Evaporation measurements in a two-phase mixture

Evaporation of droplets in a two-phase mixture is a process in which many variables change and interact simultaneously. In our new aerosol shock tube facility, we have developed a suite of wavelength-multiplexed laser diagnostics to measure the histories of droplet size distribution, droplet loading, vapor temperature and vapor pressure of two-phase water mixtures behind shock waves. Six lasers in the range of 1.330-9.569 μm have been used for these measurements. A schematic of the laser set up is shown in Fig. 10. The water and dodecane droplets considered in these experiments are in the range of 1-10 μm , and are suspended in argon. Evaporation experiments were conducted behind incident shock waves with temperatures between 450 and 650 K for water, and 500-800 K for dodecane. Measurements included characteristic droplet distribution diameter (D_{V50}) and particle loading, along with particle vapor pressure and temperature. Example particle loading data are shown in Fig. 11. From these measurements, we are able to infer rate coefficients for the D^2 evaporation law; see Fig. 12. These measurements lay the foundation for extending studies in reactive two-phase systems. This work is described more fully below and will be described in Hanson et al. (2005).

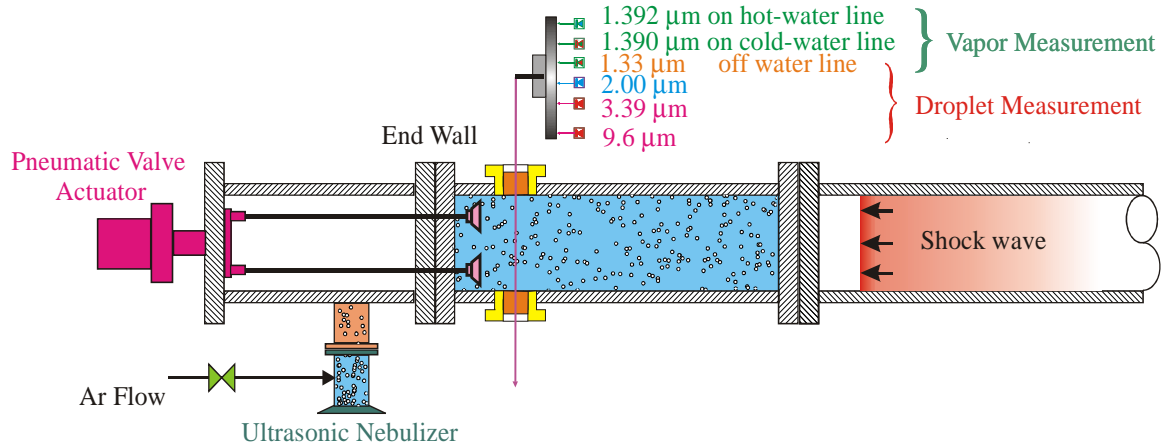


Figure 10. Cross-sectional illustration of the diagnostic setup, looking toward the endwall. Six lasers pass through the test section, thus giving line-of-sight information about the particle size distribution, gas temperature, and vapor pressure.

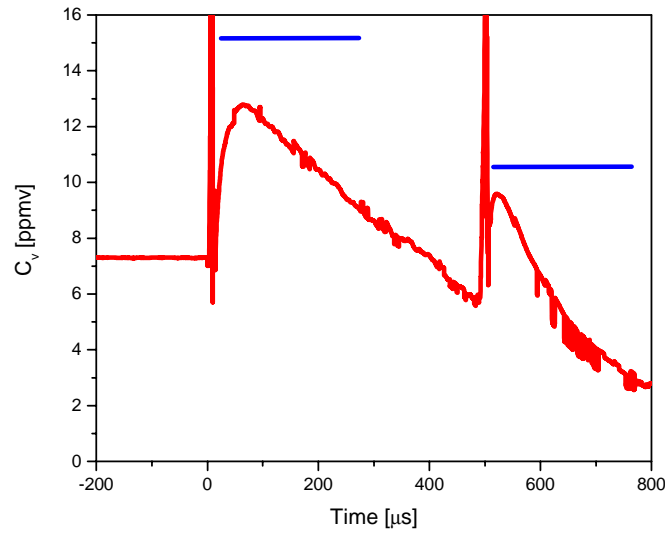


Figure 11. Typical measurement of particle loading in a shock experiment. Shock conditions: $T_1 = 293 \text{ K}$, $P_1 = 0.266 \text{ atm}$, $T_2 = 549 \text{ K}$, $P_2 = 1.102 \text{ atm}$, $T_5 = 856 \text{ K}$, $P_5 = 3.362 \text{ atm}$. The blue lines indicate the ideal gas density increases across the shocks.

Mie Extinction Diagnostic

Mie theory has been extensively applied to particle sizing. There have been several studies in shock tubes in which Mie scattering measurements were inverted to determine characteristics of the particles inside a shock tube (e.g., see Roth and Fischer (1985), Timmler and Roth (1989), Roth (1991), Hirahara and Kawahashi (1991) and Peters and Paikert (1993).) In general, the studies assume that the particles may be characterized by a single diameter. For common liquids, though, this approximation appears to cause incorrect estimations of the

particle loading. Moreover, since the size distribution is significant in the evaporation, combustion, and detonation behavior of sprays, knowing the shape of the distribution is essential.

Since the inverse scattering problem is badly conditioned, it is difficult to directly infer the particle size distribution from extinction measurements. Here we instead used the dependent model of light scattering, described in Cai, et al. (1992), where one assumes the shape of the size distribution, and then finds the distribution parameters that best fit the experimental data. The relation between single-scattered, monochromatic light with a polydisperse aerosol is given by

$$\ln\left(\frac{I}{I_o}\right) = -\frac{\pi LN}{4} \int_0^{\infty} Q_{ext}(D, \lambda, m) f(D) D^2 dD \quad (1)$$

where I is the measured intensity, I_o is the incident intensity without particles present, L is the measurement path length, N is a scaling factor related to particle loading, Q_{ext} is the Mie extinction coefficient, λ is wavelength, m is the complex refractive index, f is a normalized distribution function and D is diameter.

To perform these measurements, we used lasers at three wavelengths: two diode lasers at 1330 nm and 1997 nm, and a tunable CO₂ laser at 9569 nm. The CO₂ laser is useful because the Mie extinction coefficient changes monotonically with size for distributions including particles up to 20-30 microns, which is well beyond the diameter of our largest droplets. The signals were recorded before each run when no fog was present to accurately measure each I_o , the reference signal level for each wavelength. Then, we introduced the fog into the tube, shocked it, and recorded the intensity levels, I , for each wavelength. Since the particle loading is not known beforehand, we took ratios of the experimental data associated with different colors to remove the dependence on L and N (see Eqn. 1). Thus, the ratios are independent of the number density.

For each wavelength, we compute the logarithm of (I/I_o) from our measurements. Since the extinction coefficient is a known function, the right-hand side is a function only of the particle size distribution and wavelength. With three wavelengths, we have two independent ratios with which to make this measurement. It is common to use a two-parameter log-normal distribution to approximate aerosol size distributions. To determine what distribution best described our data, we tabulated the integral in Eqn. 1 for approximately 100,000 combinations of the two parameters and calculated the ratios that would be found for each combination. By searching for the best fit between our measurements and the table, we inferred the particle size distribution in terms of a mode and log-normal width parameter as the particles evaporated. With this, we returned to Eqn. 1 once more to determine N , and consequently, the liquid volume fraction occupied by the liquid particles.

Spectroscopic Temperature and Vapor Pressure Diagnostic

The short timescales of shock-tube experiments prevents a single laser from being scanned far and fast enough to gain the spectroscopic information we need to time-resolve the temperature and pressure of the vapor. Consequently, we have used diode lasers at three wavelengths: one coincident with a "hot" water line at 1.392 μm , a second with a "cold" water

line at 1.390 μm , and a third at an off-resonant wavelength of 1.330 μm . Since the wavelengths are close to each other, the effects of Mie scattering are nearly the same for all the lasers. Moreover, this allows us to use the measurement at the off-resonant wavelength to separate the effects due to Mie scattering from those due to vapor absorption. The two resonant colors allow determination of temperature and vapor pressure from the measurements.

D-Squared Law Evaporation Rate Constants

Since the particle volume fraction is associated with a characteristic diameter cubed, $C_v^{2/3}$ is proportional to the characteristic diameter squared. The proportionality constant is determined by assuming the characteristic diameter of the size distribution remains constant across the shock wave. With this, we are able to determine the rate constant used in the D^2 evaporation law as a function of temperature by fitting the slope of $C_v^{2/3}$ vs. time.

By performing similar experiments at various temperatures, we can observe how the evaporation rate changes with temperature. We observe that the evaporation rate constant increases with temperature behind the incident shock wave for both water and dodecane, as predicted by standard evaporation theory. Preliminary determinations of the D^2 evaporation rate coefficient are shown in Fig. 12.

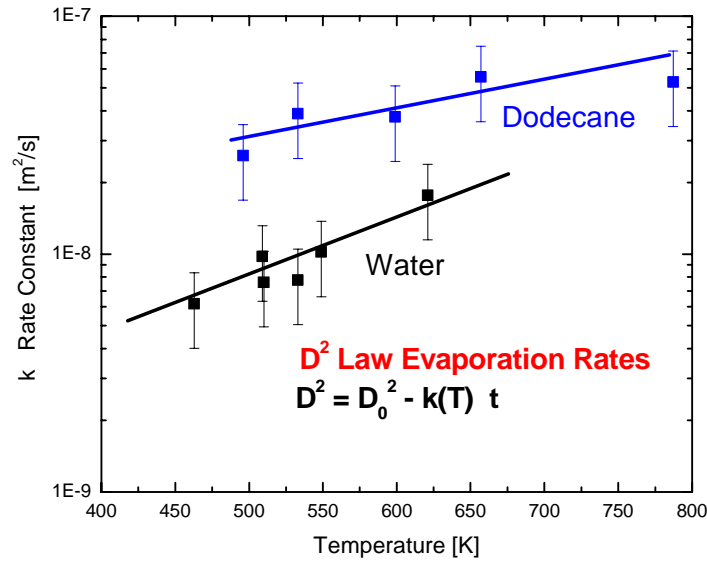


Figure 12. Rate coefficients derived from shock tube experiments for the D^2 evaporation law for water and dodecane.

Transitions

The results of the research performed under this contract have found immediate and long-term use by several groups and agencies. The ignition time measurements, in particular, are already being used extensively by the combustion community for validation and refinement of large fuel surrogate reaction mechanisms.

Several groups have used the measurements of the alkane ignition times and OH concentration time-histories in the long-term development of primary reference fuel kinetic mechanisms (C. Westbrook and W. Pitz, Lawrence Livermore National Laboratory; F. Dryer, at Princeton University; H. Wang University of Delaware), and in the development of plasma-assisted combustion models (S. Williams, AFRL).

The measurements of the branched-alkane ignition times and OH concentration time-histories have found immediate use in the current DOE EERE program for the development of HCCI (homogeneous charge compression ignition) engines (D. Assanis, University Michigan). This program strongly interacts with the automobile, truck and engine industries, and includes regular meetings with GMC and Caterpillar Corp.

Shock tube measurement techniques developed under this program have been used in our laboratory to measure to ignition times in gasoline and gasoline-surrogate fuel mixtures needed by industry for characterization of gasoline-surrogate reaction mechanisms (T. Sloan, General Motors Research and Development).

Measurements characterizing energetic ignition experiments (shock tube ignition time measurements at high fuel concentration levels that general lead to detonations) are being used in the development of computational detonation models (C. Morris, NASA Marshall Space Flight Center).

The measurements of the n-alkane ignition times, in particular those for propane, have been used by modelers at NRL (K. Kailasanath) in predicting and improving the performance of pulse detonation engines.

Mie scattering and gas phase fuel detection methods using TDL (tunable diode lasers) developed and tested in our shock-spray interaction facility for the measurement of size distribution and fuel loading have been applied to: fuel injector characterization (E. Gutmark, University of Cincinnati, ONR), and pulse detonation engine development (C. Brophy, Naval Post Graduate School, ONR).

Listing of All Publications and Technical Reports

Papers Published in Peer-Reviewed Journals

- 1) D. F. Davidson, B. M. Gauthier and R. K. Hanson, "*Shock Tube Ignition Measurements of Iso-Octane/Air and Toluene/Air at High Pressures*," Proceedings of the Combustion Institute 30, in press.
- 2) V. Venkatesh, D. F. Davidson and R. K. Hanson, "*Shock Tube Measurements of Toluene Ignition Times and OH Concentration Time-Histories*," Proceedings of the Combustion Institute 30, in press.
- 3) D. F. Davidson and R. K. Hanson, "*Interpreting Shock Tube Ignition Data*," International Journal of Chemical Kinetics 36, 510-523 (2004).
- 4) M. A. Oehlschlaeger, D. F. Davidson, J. T. Herbon, and R. K. Hanson, "*Shock Tube Measurements of Branched Alkane Ignition Times and OH Concentration Time-Histories*," International Journal Chemical Kinetics 36, 67-78 (2004).
- 5) D. F. Davidson, M. A. Oehlschlaeger, J. T. Herbon, and R. K. Hanson, "*Shock Tube Measurements of Iso-Octane Ignition Times and OH Concentration Time-Histories*," Proceedings of the Combustion Institute 29, 1205-1301 (2002).
- 6) Horning D.C., Davidson D.F., and Hanson R.K., "*Study of the High-Temperature Autoignition of n-Alkane/O₂/Ar Mixtures*," J. Propulsion Power 18: 363-371 (2002).

Papers Published in Conference Proceedings or Non-Peer-Reviewed Journals

- 1) T. C. Hanson, L. Ma, D. F. Davidson, and R. K. Hanson, "*The Dynamics of Droplet Evaporation Behind Shock Waves*," in preparation, 43rd AIAA Aerospace Sciences Meeting, Reno, January (2005).
- 2) J. T. Kashdan, T. C. Hanson, L. Ma, E. L. Piper, D. F. Davidson, and R. K. Hanson "A New Experimental Facility for the Study of Shock Wave – Induced Combustion of Liquid Fuels" AIAA Paper 2004-0468, 42nd AIAA Aerospace Sciences Meeting, Reno, January (2004).
- 3) C. S. Libby, D. F. Davidson and R. K. Hanson, "*A Shock Tube Study of the Oxidation of 1,3-Butadiene*," AIAA Paper 2004-1322, 42nd AIAA Aerospace Sciences Meeting, Reno, January (2004).
- 4) D. F. Davidson and R. K. Hanson, "*Interpreting Shock Tube Ignition Data*," Paper 03F-61, Western States Section/Combustion Institute Fall Meeting, Los Angeles (2003).

- 5) D. F. Davidson, B. M. Gauthier and R. K. Hanson, "*A Shock Tube Study of Iso-Octane and Toluene Ignition at High Pressures*," Paper 03F-26, Western States Section/Combustion Institute Fall Meeting, Los Angeles (2003).
- 6) M. A. Oehlschlaeger, D. F. Davidson, J. T. Herbon, and R. K. Hanson, "*Shock Tube Measurements of Branched Alkane Ignition Times and OH Concentration Time-Histories*," AIAA Paper 2003-0830, 41st AIAA Aerospace Sciences Meeting, Reno, January (2003).
- 7) D. C. Horning, D. F. Davidson and R. K. Hanson, "*Shock Tube Study of the High-Temperature Thermal Decomposition of n-Alkanes*," Proceedings of the 23th Shock Wave Symposium (2001).
- 8) D. C. Horning, D. F. Davidson and R. K. Hanson, "*Ignition Time Correlations for n-Alkane/O₂/Ar Mixtures*," Proceedings of the 23th Shock Wave Symposium (2001).

List of all Participating Scientific Personnel

Professor R. K. Hanson, principal investigator.

Dr. D. F. Davidson, senior research scientist.

Dr. J. Kashdan, research associate.

Dr. D. C. Horning, received Ph.D. Mechanical Engineering June 2001.

Dr. J. T. Herbon, received M. Sc. and Ph. D. Mechanical Engineering June 2004

T. C. Hanson, doctoral candidate.

L. Ma, doctoral candidate, received M. Sc. 2002.

M. A. Oehlschlaeger, doctoral candidate, received M. Sc. 2002.

E. Piper, graduate research assistant (NSF Fellow), received M. Sc. 2003.

Report of Inventions (none)

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Appendixes (none)